

Generation of metallomesogens using common ligands functionalised with liquid-crystalline moieties[§]

Induhara S. Shashikala and Duncan W. Bruce*

Department of Chemistry, University of York, Heslington, YORK YO10 5DD, UK.

Electronic Supplementary Information

[§] Dedicated to Professor Ken Wade on the occasion of his 75th birthday.

General

Some of the intermediate bipyridines were prepared using standard procedure from the literature. The hydroxyl function of 1-bromo-*x*-hydroxyalkane was protected with THP to give **1**,¹ which was then reacted with the dianion of 5,5'-dimethyl-2,2'-bipyridine (*via* reaction with LDA) at low temperature to give the coupled product, **2**² and deprotection of the alcohol led to **3**.³

Synthesis of 4-12

To a cooled 0° C and magnetically stirred solution of 5,5'-Bis(hydroxyundecyl)-2,2'-bipyridine (0.5 g, 0.95 mmol), 4'-Hydroxybiphenyl-4-carbonitrile (0.312 g, 1.90 mmol) and triphenylphosphine (0.597 g, 2.28 mmol) in dry THF (25 cm³) was added diethylazodicarboxylate (0.396 g, 2.28 mmol) drop wise over a period of 5 min under nitrogen atmosphere. The reaction mixture was allowed to attain to room temperature and was stirred for 12 h. The precipitate was filtered off and the residue was purified by recrystallization with dichloromethane/ethanol (1:9) giving a white solid. Yield 0.5 g, 60%.

Colourless solid; ¹H NMR (500 MHz, CDCl₃): δ 8.47 (s, 2H, Ar), 8.25 (AA'XX', *J* = 8 Hz, 2H, Ar), 7.66 (AA'XX', *J* = 8 Hz, 4H, Ar), 7.62-7.49 (m, 6H, Ar), 7.50 (d, *J* = 9 Hz, 4H, Ar), 6.97 (d, *J* = 7 Hz, 4H, Ar), 3.98 (t, *J* = 6.5 Hz, 4H, 2 x OCH₂), 2.64 (t, *J* = 6.4 Hz, 4H, 2 x CH₂) and 1.79-1.27 (m, 40H, 20 x CH₂); Elemental analysis C₆₀H₇₀N₄O₂: Calculated (Found): C 81.96 (81.72), H 8.02 (8.5) and N 6.37(6.30).

Preparation [PdCl₂(4-12)₂]

A solution of [PdCl₂(NCPPh)₂] (0.063 g, 0.16 mmol) and bipyridine ligand (4-12) (0.2 g, 0.23 mmol) in dry chloroform (20 ml) was heated to reflux for 16 h. Filtration and washing with methanol gave the final product as pale yellow solid. The product was further purified by recrystallisation with dichloromethane/ethanol to afford yellow solid. Yield 0.15 g, 62.5%.

Yellow solid; ¹H NMR (500 MHz, CDCl₃): δ 9.19 (s, 2H, Ar), 8.47 (AA'XX', *J* = 8 Hz, 2H, Ar), 8.22 (AA'XX', *J* = 8 Hz, 2H, Ar), 7.90 (AA'XX', *J* = 8 Hz, 4H, Ar), 7.86 (AA'XX', *J* = 8.5 Hz, 4H, Ar), 7.72 (d, *J* = 8.5 Hz, 4H, Ar), 7.07 (d, *J* = 8.5 Hz, 4H, Ar), 4.04 (t, *J* = 6.5 Hz, 4H, 2 x OCH₂), 2.75 (t, *J* = 7 Hz, 4H, 2 x CH₂) and 1.75-1.27 (m, 40H, 20 x CH₂); Elemental analysis C₆₀H₇₀ClN₄O₂Pd: Calculated (Found): C 68.21 (67.84), H 6.68 (6.64) and N 5.30 (5.27).

Preparation [PtCl₂(4-12)₂]

Equimolar amounts of the bipyridine ligand (4-12) and potassium tetrachloroplatinate in a mixture of 10 M HCl and ethanol (10:1) were heated under reflux. The yellow precipitate was collected, washed with a small amount of water and crystallised from dichloromethane/ethanol. Yield 0.145 g, 55%.

Yellow solid; ¹H NMR (500 MHz, CDCl₃): δ 9.48 (s, 2H, Ar), 7.90 (AA'XX', *J* = 8.5 Hz, 2H, Ar), 7.83 (AA'XX', *J* = 8.5 Hz, 2H, Ar), 7.66 (AA'XX', *J* = 8.5 Hz, 4H, Ar), 7.62 (AA'XX', *J* = 8.5 Hz, 4H, Ar), 7.50 (d, *J* = 9 Hz, 4H, Ar), 6.97 (d, *J* = 9.0 Hz, 4H, Ar), 3.98 (t, *J* = 6.5 Hz, 4H, 2 x OCH₂), 2.70 (t, *J* = 7 Hz, 4H, 2 x CH₂) and 1.8-1.27 (m, 40H, 20 x CH₂); Elemental analysis C₆₀H₇₀Cl₂N₄O₂Pt: Calculated (Found): C 62.93 (62.55), H 6.16 (6.13) and N 4.89 (4.80).

Preparation of [ReCl(CO)₃(4-12)]

A mixture of ligand 4-12 (0.15g, 0.17 mmol), pentacarbonylchlororhenium(I) (0.063 g, 0.17 mmol) and toluene (20 cm³) was heated under reflux for 3 h until a bright yellow-orange precipitate formed. The precipitate was recovered by filtration and crystallised from dichloromethane/hexane. Yield 0.18 g, 89%.

IR (KBr): ν_{CO}/cm⁻¹ 2013, 1909, 1900; ¹H NMR (270 MHz, CDCl₃): δ 8.61 (s, 2H, Ar), 8.24 (d, *J* = 8.5 Hz, 2H, Ar), 7.89 (d, *J* = 8.5 Hz, 2H, Ar), 7.65 (AA'XX', *J* = 8.5 Hz, 4H, Ar), 7.61 (AA'XX', *J* = 8.5 Hz, 4H, Ar), 7.50 (AA'XX', *J* = 8.6 Hz, 4H, Ar), 6.97 (AA'XX', *J* = 8.6 Hz, 4H, Ar), 3.98 (t, *J* = 6.4 Hz, 4H, 2 x OCH₂), 2.72 (t, *J* = 7.6 Hz, 4H, 2 x CH₂) and 1.8-1.27 (m, 40H, 20 x CH₂). Elemental analysis C₆₃H₇₀ClN₄O₅Re: Calculated (Found): C 63.86 (63.48), H 5.95 (5.91) and N 4.73 (4.64).

Preparation of [ZnCl₂(4-12)]

Ligand (4-12) (0.1g, 0.116 mmol) was dissolved in THF (10 cm³) to which was added zinc chloride (0.016 g, 0.116 mmol). The colourless solution was heated under reflux for 2 h under a nitrogen atmosphere. The reaction mixture was cooled to room temperature but no precipitate was observed, so hexane was added to reaction mixture resulting in the formation of a colourless precipitate. The precipitate was recovered by filtration and crystallised from dichloromethane/hexane. Yield 0.1 g, 87%.

¹H NMR (400 MHz, CDCl₃): δ 8.61 (s, 2H, Ar), 8.24 (d, *J* = 8.2 Hz, 2H, Ar), 7.89 (d, *J* = 8.0 Hz, 2H, Ar), 7.66 (AA'XX', *J* = 8.5 Hz, 4H, Ar), 7.61 (AA'XX', *J* = 8.5 Hz, 4H, Ar), 7.50 (AA'XX', *J* =

8.7 Hz, 4H, Ar), 6.96 (AA'XX', $J = 8.7$ Hz, 4H, Ar), 3.98 (t, $J = 6.4$ Hz, 4H, 2 x OCH₂), 2.72 (t, $J = 7.6$ Hz, 4H, 2 x CH₂) and 1.8-1.27 (m, 40H, 20 x CH₂). Elemental analysis C₆₀H₇₀Cl₂N₄O₂Zn: Calculated (Found): C 70.96 (70.99), H 5.52 (5.36) and N 6.95 (7.00).

Preparation of 4-(6'-bromohexyloxy)acetophenone (7)

A mixture of 1,6-dibromohexane (5 g, 36.36 mmol), 4-hydroxyacetophenone (35.7g, 147 mmol), sodium bicarbonate (14.7 g, 147 mmol), a catalytic amount of potassium iodide and acetone (100 cm³) was heated under reflux for 24 h. The product obtained on evaporation of the solvent was poured into water and extracted with dichloromethane (2 x 100 cm³). The combined organic extracts were washed with brine and dried over Na₂SO₄. Evaporation of the solvent furnished the crude product which was distilled to remove excess of 1,6-dibromohexane. The pure compound was then obtained as a colourless solid by crystallisation of the residue from a mixture of dichloromethane/ethanol. Yield: 8.1 g; 73.6 %.

¹H NMR (270 MHz, CDCl₃): δ 7.74 (AA'XX', $J = 8.9$ Hz, 2H, Ar), 6.74 (AA'XX', $J = 8.9$ Hz, 2H, Ar), 3.95-3.78 (m, 2H, 1 x OCH₂), 3.17-2.94 (m, 2H, 1 x CH₂), 2.27 (s, 3H, 1 x -CH₃), and 1.8-1.4 (m, 8H, 4 x CH₂).

Preparation of methyl 4-(6'-bromohexyloxy)benzoate (8)

A mixture of 1,6-dibromohexane (5g, 32.6 mmol), methyl 4-hydroxybenzoate (31.7g, 130.7 mmol), sodium bicarbonate (13.7 g, 130.7 mmol), a catalytic amount of potassium iodide and acetone (100 cm³) were heated under reflux for 24 h. The product obtained on evaporation of the solvent was poured into water and extracted with dichloromethane (2 x 100 cm³). The combined organic extracts was washed with brine and dried over Na₂SO₄. Evaporation of the solvent furnished the crude product which was distilled to remove excess of 1,6-dibromohexane. The pure compound was obtained as a colourless solid by crystallisation of the residue from a mixture of dichloromethane/ethanol. Yield: 8.5 g, 80%.

¹H NMR (270 MHz, CDCl₃): δ 7.95 (AA'XX', $J = 8.9$ Hz, 2H, Ar), 6.87 (AA'XX', $J = 8.9$ Hz, 2H, Ar), 4.01-3.98 (m, 2H, 1 x OCH₂), 3.96 (s, 3H, 1 x -OCH₃), 3.40-3.38 (m, 2H, 1 x CH₂) and 1.8-1.4 (m, 8H, 4 x CH₂).

Preparation of 9

A mixture of 4-(6'-bromohexyloxy)acetophenone (1.8 g, 6.15 mmol), 4'-hydroxybiphenyl-4-carbonitrile (1 g, 5.12 mmol), potassium carbonate (2.8 g, 20.5 mmol) and dimethylformamide (20 cm³) were heated at 80 °C under a nitrogen atmosphere for 16 h. The reaction mixture was poured

into ice-cold water, precipitating a colourless solid, which was filtered, washed and crystallised from a mixture of dichloromethane/ethanol. Yield: 2.2 g; 92%.

^1H NMR (270 MHz, CDCl_3): δ 7.92 (AA'XX', $J = 8.9$ Hz, 2H, Ar), 7.66 (AA'XX', $J = 8.4$ Hz, 2H, Ar), 7.62 (AA'XX', $J = 8.4$ Hz, 2H, Ar), 7.50 (AA'XX', $J = 8.5$ Hz, 2H, Ar), 6.97 (AA'XX', $J = 8.5$ Hz, 2H, Ar), 6.90 (AA'XX', $J = 8.9$ Hz, 2H, Ar), 4.02 (q, $J = 6.75$ Hz, 4H, 2 x -OCH₂), 2.53 (s, 3H, 1 x -CH₃), 1.93-1.76 (m, 4H, 2 x -CH₂) and 1.65 -1.48 (m, 4H, 2 x -CH₂).

Synthesis of Compound 10

A mixture of methyl 4-(6'-bromohexyloxy)benzoate (2.0 g, 6.15 mmol), 4'-hydroxybiphenyl-4-carbonitrile (1 g, 5.12 mmol), potassium carbonate (2.8 g, 20.5 mmol) and dimethylformamide (20 cm³) were heated at 80 °C under nitrogen atmosphere for 16 h. The reaction mixture was poured into ice cold water, precipitating a colourless solid, which was filtered, washed and crystallised from a mixture of dichloromethane/ethanol. Yield: 2 g; 80%.

^1H NMR (270 MHz, CDCl_3): δ 7.96 (AA'XX', $J = 8.8$ Hz, 2H, Ar), 7.67 (AA'XX', $J = 8.4$ Hz, 2H, Ar), 7.61 (AA'XX', $J = 8.4$ Hz, 2H, Ar), 7.51 (AA'XX', $J = 8.7$ Hz, 2H, Ar), 6.97 (AA'XX', $J = 8.7$ Hz, 2H, Ar), 6.89 (AA'XX', $J = 8.8$ Hz, 2H, Ar), 4.02 (q, $J = 6.75$ Hz, 4H, 2 x -OCH₂), 3.86 (s, 3H, 1 x -OCH₃), 1.93-1.76 (m, 4H, 2 x -CH₂) and 1.65 -1.48 (m, 4H, 2 x -CH₂).

Synthesis of Compound 11

To a mixture of **8** (1 g, 2.14 mmol) and **10** (1.03 g, 2.14 mmol) in dimethoxyethane (100 cm³), a dispersion of NaH in mineral oil (60%, 0.25 g, 10.7 mmol) was added in small portions. When the effervescence ceased, the mixture was heated under reflux for 3 h with vigorous stirring. The mixture was allowed to cool to room temperature and acidified with dilute hydrochloric acid, giving rise to pale orange precipitate. The precipitate was filtered, washed with water and crystallised from a mixture of dichloromethane/ethanol (50:50) to afford the product as a yellow solid. Yield 1.6 g, 94%.

^1H NMR (400 MHz, CDCl_3): δ 17.13 (s, 1H, 1 x OH), 7.92 (d, $J = 8.9$ Hz, 4H, Ar), 7.67 (d, $J = 9.2$ Hz, 4H, Ar), 7.61 (d, $J = 8.4$ Hz, 4H, Ar), 7.51 (d, $J = 8.5$ Hz, 4H, Ar), 6.95 (t, $J = 8.5$ Hz, 8H, Ar), 6.70 (s, 1H, 1 x -CH=C), 4.02 (q, $J = 6.75$ Hz, 8H, 4 x -OCH₂), 1.93-1.76 (m, 8H, 4 x -CH₂) and 1.65 -1.48 (m, 8H, 4 x -CH₂); Elemental analysis C₅₃H₅₀N₂O₆: Calculated (Found): C 78.49 (78.01), H 6.21 (6.23) and N 3.45 (3.32).

Preparation of copper complex, 12

A solution of compound **11** (100 mg, 0.12 mmol) dissolved in dichloromethane (15 cm³) was mixed with methanol solution (5 cm³) of copper(II) acetate (11.9 mg, 0.06 mmol) under a nitrogen atmosphere. The resulting mixture was heated under reflux for 2 h until a green precipitate was observed. The mixture was cooled and precipitate was filtered, washed with water and crystallised from a mixture of dichloromethane/hexane. Yield: 0.18 g; 87%.

Elemental analysis C₁₀₆H₉₈CuN₄O₁₂: Calculated (Found): C 75.63 (75.29), H 5.87 (5.80) and N 3.33 (3.12).

Preparation of iridium complex, 14

A mixture of compound **11** (150 mg, 0.185 mmol), potassium carbonate (255 mg, 1.85 mmol), chloro-1,5-cyclooctadieneiridium (I) dimer (62.2 mg, 0.092 mmol) and THF (20 cm³) were placed in a 25 cm³ Schlenk flask and stirred at room temperature for 5 h under an argon atmosphere. The reaction mixture was evaporated to dryness and was redissolved THF (20 cm³); the solution was then cannula filtered to remove insoluble materials. Carbon monoxide was then bubbled through the solution for 15 minutes. The solvent was then removed under reduced pressure and the product was crystallised from dichloromethane/ethanol, affording green solid, which was further purified using column chromatography (silica gel, 100-200 mesh) with dichloromethane as eluant. An orange solid resulted in exceptionally low yield as most of the material became stuck on the column.

Yellow solid; ¹H NMR (400 MHz, CDCl₃): δ 7.87 (AA'XX', *J* = 8.8 Hz, 4H, Ar), 7.61 (AA'XX', *J* = 8.6 Hz, 4H, Ar), 7.56 (AA'XX', *J* = 8.4 Hz, 4H, Ar), 7.45 (AA'XX', *J* = 8.8 Hz, 4H, Ar), 6.92 (m, 5H, 4Ar, 1 x -CH=C), 6.87 (AA'XX', *J* = 8.8 Hz, 3H, Ar), 3.98-3.94 (m, 8H, 4 x -OCH₂), 1.80-1.76 (m, 8H, 4 x -CH₂) and 1.58 -1.43 (m, 8H, 4 x -CH₂). IR (cm⁻¹): ν_{CO}: 2069 and 1993. Elemental analysis C₅₅H₄₉IrN₂O₈: Calculated (Found): C 62.43 (62.87), H 4.67 (5.03) and N 2.65 (2.63).

Preparation of vanadium complex, 13

Compound **11** (100 mg, 0.123 mmol) was added to a minimum amount of dichloromethane (5 cm³) in which it did not dissolve completely. Oxovanadium(IV) sulfate (20 mg, 0.123 mmol) was dissolved in one drop of water followed by the addition of methanol (10 ml) and was heated under reflux under a nitrogen atmosphere. The partially dissolved ligand in dichloromethane was then added to the hot vanadium containing solution and this was followed by the addition of potassium hydroxide (3.5 mg, 0.06 mmol). The reaction mixture was heated under reflux for a further period of 4 h. A greenish yellow precipitate was observed which was filtered hot and washed with

methanol. Crystallisation from a mixture of dichloromethane and ethanol afforded a pure product. Yield: 0.158 g; 76%.

Elemental analysis C₁₀₆H₉₈N₄O₁₃V: Calculated (Found): C 75.47(74.39), H 5.86 (5.74) and N 3.32 (3.45). Data for this complex were consistently outside normally acceptable limits. Nonetheless, the clearing point was quite sharp and we do not believe that the discrepancy alters the phase behaviour nor any of the broader points made in the paper.

Preparation of *orthopalladated* complex, 15

Compound **11** (100 mg, 0.123 mmol) was dissolved in dichloromethane (10 cm³) and a drop of triethylamine was added; the reaction mixture was stirred at room temperature for 5 min under nitrogen. Di(*μ*-acetato)bis(benzylideneaniline)dipalladium(II) (34 mg, 0.061 mmol) was dissolved in dichloromethane (10 cm³) and then added slowly to the reaction mixture and then stirred at room temperature for 5 h under nitrogen. The reaction mixture was filtered and evaporated to dryness. Crystallisation from a mixture of dichloromethane/ethanol afforded the product as a yellow solid. Yield 0.095 g, 70%.

¹H NMR (400 MHz, CDCl₃): δ 8.16 (s, 1H, -CH=N), 7.97 (AA'XX', $J = 8.6$ Hz, 2H, Ar), 7.78 (AA'XX', $J = 7.64$ Hz, 1H, Ar), 7.65-7.62 (m, 10H, Ar), 7.51-7.45 (m, 10H, Ar), 7.31-7.24 (m, 1H, Ar), 7.15-7.11 (m, 1H, Ar), 6.95 (t, $J = 8.6$ Hz, 6H, Ar), 6.77 (AA'XX', $J = 8.8$ Hz, 2H, Ar), 6.61 (s, 1H, -CH=C), 4.01-3.99 (m, 8H, 4 x OCH₂), 1.92-1.75 (m, 8H, 4 x CH₂) and 1.62-1.48 (m, 8H, 4 x CH₂); Elemental analysis C₆₀H₇₀ClN₄O₂Pd: Calculated (Found): C 72.29 (72.32), H 5.42 (5.61) and N 3.83 (3.87).

- 1 M. T. Reetz, C. J. Rüggeberg, M. J. Dröge and W. J. Quax, *Tetrahedron Letts.*, 2002, **58**, 8465.
- 2 K. E. Amos, *PhD Thesis*, University of Exeter, 2005 and K. R. Seddon and Y. Z. Yousif, *Tran. Met. Chem.*, 1986, 443.
- 3 S. D. Feyter, M. M. S. Abdel-Mottaleb, N. Schuurmans, B. J. V. Verkuijl, J. H. Van Esch, B. L. Feringa and F. C. Schryver, *Chem. Eur. J.*, 2004, **10**, 1124.